Nucleation rate in supersaturated vapors

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(With 4 Figures in Text.)

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1 Introduction

When it comes to the question of the formation of a new stable phase from a supersaturated one, the frequency with which nuclei form is of primary interest. This view underlies almost all work that has dealt with the kinetics of the formation of a new phase, partly theoretically and partly experimentally. A nucleus was understood to be a small, spontaneously formed preferred droplet or crystal from which the visible particles of the new phase form as they grow.

Until recently, there were no quantitative approaches to the size of the nucleus and its possible connection to the supersaturation pressure. The nucleus received a physical meaning through VOLMER and WEBER's definition[1], which understands by nucleus a droplet or crystal that has the same vapor pressure as the supersaturation pressure. This nucleus is in equilibrium with the supersaturated phase. This also determines the size of the nucleus, and a very specific amount of work ε is required to produce this characteristic droplet inside the homogeneous vapor. This work was already calculated by GIBBS using thermodynamic methods and, in addition to the supersaturation pressure, depends on the capillary forces between the nucleus and the vapor. It is

$$\varepsilon = \frac{1}{3} \mathscr{F} \cdot \sigma ,$$

where $\mathscr{F}$ is the surface of the nucleus and σ its surface tension.

VOLMER and WEBER were the first to make an approach to the number of nuclei present in a supersaturated vapor in which, based on EINSTEIN's general thermodynamic considerations[2], they estimated the stationary number of nuclei on the order of

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[1] VOLMER and WEBER, Keimbildung in übersättigten Gebilden. Zeitschr. f. physik. Chemie **119**, 277 (1926).

[2] A. EINSTEIN, Ann. d. Physik **33**, 1275 (1910)

$$\varkappa = C \cdot e^{-\frac{\mathscr{F}\cdot\sigma}{3kT}} .$$

Furthermore, in the cited work by VOLMER and WEBER it is assumed that the number of nuclei that grow into visible structures per second is proportional to the stationary number of nuclei. The model is the ARRHENIUS theory of the reaction rate, where the activation heat plays the same role as the characteristic work here: ε.

The aim here is to show that the above approach can be precisely justified on the basis of simple kinetic ideas and that the number of droplets that grow into a visible structure can be calculated from the stationary number of nuclei.[3].

2 Theoretical Considerations

We want to limit ourselves to the case of supersaturated vapor, since the conditions are simplest here.

Our basic assumption is that as a result of the collisions of the molecules in the vapor space, some molecules can combine, and that the particle number n or the radius x of the resulting droplet is subject to irregular size changes as a result of natural fluctuations. The change in the number of particles or the radius occurs either by capturing one molecule or by emitting another, and since the probability of these processes is generally not the same, the fluctuation of n will be subject to laws similar to those for the movement of a particle in BROWN'ian motion in a force field. The whole problem could be illustrated by the following picture. In a vessel, specifically heavier particles are suspended in a liquid. These will assume a hypsometric distribution due to the fluctuations in the gravity field[4]. A certain number of particles is at the height n_0 – that is the stationary number of nuclei. A force is now supposed to act in this cross section that pulls the nuclei upwards. The stationary distribution is superimposed by a downward and upward diffusion of the particles. The particles that diffuse upwards to large n values give the number of droplets that grow into visible structures. Now, in every diffusion problem, in order to be able to calculate the number of particles migrating through a cross section, the concentration must be given at two points. In our case, the downward diffusion must not disturb the stationary distribution, so the equilibrium concentration prevails at the bottom, but the concentration of the droplets must vanish at the top for very large n.

We now want to follow what has been said here mathematically and calculate the number of droplets with the number of molecules n per cm^3.

The vapor pressure of the droplet is a function of n due to surface tension, and we

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[3] The idea underlying the strict treatment stems from L. SZILÁRD.

[4] A. EINSTEIN, Ann. d. Physik **19**, 371 (1906)

will denote it by $p(n)$. Until $p(n)$ is greater than the supersaturation pressure p_r, the stationary state prevails, i.e. on average as many droplets with the number of molecules n will form as will disappear through evaporation during this time. This will be the case for all droplets whose particle number is below n_0. The elementary process is always that a droplet captures an impacting molecule or loses one through evaporation.
Let the number of droplets with n molecules be $Z(n)$, then the following equation must apply to the stable state under consideration:

$$\alpha \cdot p_r \cdot Z(n) \cdot \mathscr{F}(n) = \alpha \cdot p(n+1) \cdot Z(n+1) \cdot \mathscr{F}(n+1)\,,$$

if $\alpha \cdot p_r$ is the number of molecules, which are separated at $1\,\mathrm{cm}^2$ per second, $\alpha \cdot p(n)$ the number of molecules, which are emitted at $1\,\mathrm{cm}^2$ per second and if $\mathscr{F}(n)$ or $\mathscr{F}(n+1)$ respectively is the surface of the droplets. We define

$$\begin{aligned} Z'(n) &= Z(n) \cdot \mathscr{F}(n) \\ Z'(n+1) &= Z(n+1) \cdot \mathscr{F}(n+1)\,. \end{aligned}$$

For $p(n+1)$ we can set as a good approximation $p(n)$. We therefore have:

$$\frac{Z'(n+1)}{Z'(n)} = \frac{p_r}{p(n)}\,,$$

or, if we make a transformation to ln:

$$\frac{\ln\left[Z'(n+1)\right] - \ln\left[Z'(n)\right]}{1} = \ln\left(\frac{p_r}{p(n)}\right)\,.$$

From this equation we obtain a differential equation for $Z'(n)$ if we set $1 = \mathrm{d}n$. For reasonably large n this is justified. The differential equation then reads:

$$\frac{\mathrm{d}\ln\left[Z'(n)\right]}{\mathrm{d}n} = \ln\left(\frac{p_r}{p(n)}\right)\,. \tag{1}$$

To integrate the differential equation, we need to know $p(n) = p(x)$ as a function of n or of the corresponding radius x.
If we use p_∞ to denote the saturation pressure of a flat surface at temperature T, the following relationship applies:

$$\mathscr{R}T \cdot \ln\left(\frac{p(x)}{p_\infty}\right) = \frac{2\sigma M}{x\gamma} \quad \text{or} \quad p(x) = p_\infty \cdot e^{\frac{2\sigma M}{x\gamma \mathscr{R} T}}\,, \tag{2}$$

where M is the molecular weight, γ the specific weight of the droplet. This derivation assumes that the surface tension σ is independent of x, but this is certainly not the case if one goes to droplets that are so small that the sphere of action of one molecule is not completely filled with others. We will use the equation in this form anyway, which is certainly valid up to about $5 \times 10^{-7}\,\mathrm{cm}^5$, but deviations can occur at radii of molecular size.

$p(x) = p_r$ corresponds to a certain radius $x = r$; this is the radius of the characteristic droplet. Its size is determined by the degree of supersaturation. We can express the stationary number of nuclei n_0 or generally the particle number n by r or x:

$$n = \frac{4\pi}{3} \cdot x^3 \cdot \frac{\gamma}{M} \cdot L\,, \tag{3}$$

where L is the Loschmidt number, $= 6,06 \cdot 10^{23}$, and

$$\frac{\mathrm{d}n}{\mathrm{d}x} = \frac{4\pi x^2 \gamma \cdot L}{M}\,. \tag{4}$$

Now it is:

$$\ln\left(\frac{p_r}{p(x)}\right) = -\ln\left(\frac{p(x)}{p_r}\right) = -\ln\left(\frac{p(x)}{p_\infty}\right) + \ln\left(\frac{p_r}{p_\infty}\right)\,. \tag{5}$$

Introducing Equation 2, Equation 3, Equation 4 and Equation 5 in Equation 1 yields:

$$\frac{\mathrm{d}\ln\left[Z'(n)\right]}{\mathrm{d}n} = \frac{\mathrm{d}\ln\left[Z'(n)\right]}{\mathrm{d}x} \cdot \frac{M}{4\pi x^2 \gamma \cdot L} = -\frac{2\sigma M}{\mathscr{R} T x \gamma} + \ln\left(\frac{p_r}{p_\infty}\right)\,,$$

or

$$\frac{\mathrm{d}\ln\left[Z'(n)\right]}{\mathrm{d}x} = -\frac{8\pi x \sigma}{kT} + \frac{4\pi x^2 \cdot \frac{\gamma}{M} \cdot \mathscr{R} T \cdot \ln\left(\frac{p_r}{p_\infty}\right)}{kT}\,.$$

By integration for x we get the function we are looking for:

$$Z'(n) = \mathscr{F}(n) \cdot Z(n) = C \cdot \exp\left\{-\frac{4\pi x^2 \sigma + \frac{4\pi\gamma}{3M} \cdot x^3 \mathscr{R} T \cdot \ln\left(\frac{p_r}{p_\infty}\right)}{kT}\right\}\,.$$

One can also write it a little differently if one introduces the characteristic radius. Then:

$$Z'(n) = \mathscr{F}(n) \cdot Z(n) = c \cdot \exp\left\{-\frac{4\pi x^2 \sigma}{kT} \cdot \left(1 - \frac{2}{3}\frac{x}{r}\right)\right\}\,,$$

or $Z(n)$ itself, the number of droplet with n molecules per cm^3:

$$Z(n) = \frac{C}{\mathscr{F}(n)} \cdot \exp\left\{-\frac{4\pi x^2 \sigma}{kT} \cdot \left(1 - \frac{2}{3}\frac{x}{r}\right)\right\}\,.$$

The constant in front of the e-power is kept as unknown because one cannot use the usual integration because the formula is not valid in a significant area of the appropriate range.

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[5] van der Waals-Kohnstamm, Lehrbuch der Thermodynamik.

However, the droplets whose radius have reached r will behave differently than the droplets that have a $p(n) > p_r$. By occasionally adsorbing molecules, they will be stabilized as their pressure drops below p_r, and they will quickly grow into visible structures. According to our picture given at the beginning, this corresponds to the force that acts on the droplets in the cross section n_0 and pulls them upwards. Our Equation 1 will no longer apply to this n region, since there is no longer a stationary distribution in the latter.
$\alpha \cdot p_r \cdot \mathscr{F}(n) \cdot Z(n)$ will be greater than $\alpha \cdot F(n+1) \cdot p(n+1) \cdot Z(n+1)$ and the excess is nothing more than the number of particles migrating through the cross section n_0 towards larger n:

$$J = Z(n) \cdot p_r \cdot \alpha \cdot \mathscr{F}(n) - Z(n+1) \cdot \alpha \cdot p(n+1) \cdot \mathscr{F}(n+1)\,.$$

We set:

$$p(n) = p(n+1)\,.$$

By J we mean the number of droplets formed per second. We can reformulate this equation by adding and subtracting $\alpha \cdot p(n) \cdot \mathscr{F}(n) \cdot Z(n)$. This yields:

$$-J = [Z'(n+1) - Z'(n)] \cdot p(n) \cdot \alpha + Z'(n) \cdot \alpha \cdot [p(n) - p_r]\,. \tag{6}$$

We don't need to take the ln now, but the equation already approximately represents a differential equation, since $Z'(n)$ does not vary much with n in this range:

$$\frac{J}{\alpha \cdot p(n)} = \frac{\mathrm{d}Z'(n)}{\mathrm{d}n} + Z'(n) \cdot \frac{p(n) - p_r}{p(n)}\,. \tag{6'}$$

If we put for shortness:

$$\frac{p(n) - p_r}{p(n)} \sim \frac{p(n) - p_r}{p_r} = \varphi(n)$$

we get the linear differential equation:

$$\frac{\mathrm{d}Z'(n)}{\mathrm{d}n} + \varphi(n) \cdot Z'(n) + \frac{J}{\alpha \cdot p(n)} = 0\,,$$

which has the solutions:

$$Z'(n) = \exp\left\{-\int_{n_0}^{n} \varphi(n)\,\mathrm{d}n\right\} \cdot \left[B - \int_{n_0}^{n} \frac{J}{\alpha \cdot p(n)} \cdot \exp\left\{+\int_{n_0}^{n} \varphi(n)\,\mathrm{d}n\right\} \mathrm{d}n\right]\,.$$

$\varphi(n)$ can be approximated for the small range $n - n_0 = \mu$ with the following functions, namely for positive μ:

$$\varphi(n) = \frac{p(n) - p_r}{p_r} = -a^2 \cdot (n - n_0) = -a^2 \cdot \mu\,, \tag{7}$$

for negative μ:

$$\varphi(n) = \ln\left(\frac{p(n)}{p_r}\right) . \tag{8}$$

$\alpha \cdot p(n)$ changes even less with n, since the condensation of a molecule hardly changes the surface area and the vapor pressure. So we can take $\frac{J}{\alpha \cdot p(n)}$ in front of the integral and set $p_r = p(n)$.

In Equation 6 $-a^2$ is the slope of the curve at the point $n = n_0$ or $x = r$, $\mu = 0$. One can calculate $-a^2$ from the curve $\varphi(n)$:

$$\begin{aligned}
-a^2 &= \left[\frac{\mathrm{d}}{\mathrm{d}n}\varphi(n)\right]_{n=n_0} = \left(\frac{\mathrm{d}}{\mathrm{d}n}\left(\frac{p(n)-p_r}{p_r}\right)\right)_{n=n_0} = \left(\frac{\mathrm{d}}{\mathrm{d}n}\ln\left[\frac{p(n)}{p_r}\right]\right)_{n=n_0} \\
-a^2 &= \left(\frac{\mathrm{d}}{\mathrm{d}n}\left(\ln(p_\infty)\cdot e^{\frac{2\sigma M}{x\gamma \mathscr{R} T}}\right)\right)_{n=n_0} = \left(\frac{\mathrm{d}}{\mathrm{d}n}\left(\frac{2\sigma M}{x\gamma \mathscr{R} T}\right)\right)_{n=n_0} \\
-a^2 &= \left(\frac{\mathrm{d}}{\mathrm{d}x}\frac{2\sigma M}{x\gamma \mathscr{R} T}\cdot\frac{\mathrm{d}x}{\mathrm{d}n}\right)_{x=r} \\
-a^2 &= \left\{-\frac{2\sigma M}{x^2\gamma \mathscr{R} T}\cdot\frac{M}{4\pi x^2\gamma\cdot L}\right\}_{x=r}
\end{aligned}$$

We therefore find:

$$a^2 = \frac{8\pi\sigma M^2}{\gamma^2 \mathscr{F}^2 \mathscr{R} T\cdot L}$$

or for a itself after some rearrangement:

$$a = \ln\left(\frac{p_r}{p_\infty}\right)\cdot\sqrt{\frac{kT}{2\sigma\mathscr{F}}} , \tag{9}$$

where $\mathscr{F}$ is the surface of the characteristic droplet, $-a^2$ is of the order of magnitude 10^{-2} for water at $T = 300\,^\circ\mathrm{C}$.

In the solution of the differential equation, after we have taken $\frac{J}{\alpha \cdot p(n)}$ in front of the integral, the following integral $\int_0^\mu e^{-\frac{a^2\mu^2}{2}}\,\mathrm{d}\mu$ remains to evaluate. However, we can extend this probability integral to ∞ instead of μ, because the weight of the integral is between 0 and μ:

$$\int_{n_0}^{n} e^{-\int\varphi(n)\,\mathrm{d}n} = \int_0^\mu e^{-\frac{a^2\mu^2}{2}}\,\mathrm{d}\mu = \int_0^\infty e^{-\frac{a^2\mu^2}{2}}\,\mathrm{d}\mu = \frac{1}{a}\cdot\sqrt{\frac{\pi}{2}}$$

and therefore we get:

$$Z'(n) = e^{\frac{a^2\mu^2}{2}}\cdot\left(B - \frac{J}{\alpha\cdot p(n)\cdot a}\cdot\sqrt{\frac{\pi}{2}}\right)$$

and if we put

$$\frac{1}{\alpha\cdot p(n)\cdot a}\cdot\sqrt{\frac{\pi}{2}} = A$$

is follows that

$$Z'(n) \cdot e^{-\frac{a^2\mu^2}{2}} = B - J \cdot A \,.$$

To determine the two constants in the solution of the differential equation, we introduce the following boundary conditions. For large positive μ $Z'(n)$ must vanish and even more so $Z'(n) \cdot e^{-\frac{a^2\mu^2}{2}}$, so it follows:

$$B - J \cdot A = 0 \,.$$

On the other hand, for negative μ, $Z'(-\mu)$ transforms into the equilibrium distribution. We get, because:

$$\int_0^{-\mu} e^{-\frac{a^2\mu^2}{2}}\, \mathrm{d}\mu = \int_0^{\infty} e^{-\frac{a^2\mu^2}{2}}\, \mathrm{d}\mu = -\frac{1}{a} \cdot \sqrt{\frac{\pi}{2}}$$

and therefore:

$$B + J \cdot A = Z'(-\mu) \cdot e^{-\frac{a^2\mu^2}{2}} \,.$$

But one can proof that:

$$Z'(-\mu) \cdot e^{-\frac{a^2\mu^2}{2}} = Z'(n_0) \,,$$

namely

$$Z'(-\mu) = \exp\left\{ \int_0^{n_0 - n} \ln\left(\frac{p_r}{p(n)}\right) \mathrm{d}n \right\} \,, \quad e^{-\frac{a^2\mu^2}{2}} = \exp\left\{ \int_0^{n_0 - n} \ln\left(\frac{p(n)}{p_r}\right) \mathrm{d}n \right\}$$

and therefore:

$$Z'(-\mu) \cdot e^{-\frac{a^2\mu^2}{2}} = \exp\left\{ \int_0^{n_0} \ln\left(\frac{p(n)}{p_r}\right) \mathrm{d}n \right\} = Z'(n_0) \,. \tag{10}$$

Thus, we get for J:

$$J = \frac{Z'(n_0)}{2A} = \frac{C}{2A} \cdot e^{-\frac{4\pi r^2 \sigma}{kT} \cdot \frac{1}{3}} = \frac{C}{2A} \cdot e^{-\frac{\mathscr{F}\sigma}{3kT}} \,,$$

or, if we substitute for A its value and since $\alpha \cdot p_r$ is the average number of collisions per cm^2 and second according to the kinetic gas theory:

$$\alpha \cdot p_r = L \cdot p_r \cdot \frac{1}{\sqrt{2\pi \mathscr{R} T M}} \tag{11}$$

we have for J as a final result:

$$\boxed{J = \frac{p_r}{2\pi \mathscr{F}} \cdot C \cdot \sqrt{\frac{L \cdot \mathscr{F}}{2\sigma M}} \cdot \ln\left(\frac{p_r}{p_\infty}\right) \cdot e^{-\frac{\mathscr{F} \cdot \sigma}{3kT}}} \,, \tag{12}$$

or, after some minor rearrangement:

$$J = \frac{p_r \cdot C}{F\gamma \mathscr{R} T} \cdot \sqrt{\frac{2\sigma L M}{\pi}} \cdot e^{-\frac{\mathscr{F}\cdot\sigma}{3kT}} = \frac{p_r}{\mathscr{F}} \cdot C' \cdot e^{-\frac{\mathscr{F}\cdot\sigma}{3kT}} .$$

This is the number of drops formed per second, which remains constant as long as the initial conditions are noticeably maintained. It is hereby strictly proven that it is proportional to the number of nuclei that would be present in a stationary state if no further growth would occur, in accordance with the assumption made by Volmer and Weber. In addition, it was possible to specify the factor by which this number must be multiplied in order to obtain the reaction rate, namely the drop formation per second.

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